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(54) Curable compounds containing reactive groups: triazine/isocyanurates, cyanate esters and blocked isocyanates

(57) This invention is directed to compounds that can be used as antioxidants for exposed metal surfaces, and also as adhesion promoters for adhesive, coating or encapsulant resins that are applied to the metal substrates. These compounds include triazine or isocyanu-

rate compounds bearing reactive or polymerizable functional groups, polyfunctional cyanate esters, and poly-functional blocked-isocyanates.

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Description**FIELD OF THE INVENTION**

5 [0001] This invention relates to triazine compounds, isocyanurate compounds, cyanate ester compounds, or blocked isocyanate compounds that can act as anti-oxidants for metal substrates or metal surfaces, and particularly for copper, to improve the adhesion between metal substrates and adhesives, coatings or encapsulants.

BACKGROUND OF THE INVENTION

10 [0002] In the assembly of a semiconductor package to a printed wire board, an integrated circuit chip is attached to a metal lead frame, in many case, a copper coated leadframe, with adhesive and wire bonding, and the whole assembly then encapsulated in a molding resin. After encapsulation, the outer leads of the lead frame are attached to a printed circuit board. During storage and transportation, any metal, and particularly, copper surfaces are subject to oxidation
15 with exposure to air. Such uncontrolled oxidation is detrimental to adhesion between the lead frame and any adhesive or molding compound, and subsequently detrimental to the reliability of the whole lead frame package. To alleviate this problem, lead frame manufacturing routinely includes a process to apply an antioxidant coating onto the lead frame surface.

20 [0003] Nitrogen-containing compounds such as benzotriazoles are commonly used as antioxidants and corrosion inhibitors for copper and copper alloys in many environments and applications. The aromatic moiety of the benzotriazoles is believed to help reinforce a parallel alignment onto the metal substrate and the nitrogen rich triazole to serve as an adhesion promoter. When benzotriazole is applied as a coating, the copper surface is blocked from direct contact with air and moisture, which inhibits oxidation to certain level. However, the presence of benzotriazoles is suspected of interfering with the bonding process during the die attach, wire bonding, encapsulation, and final soldering operations
25 in the manufacture of the semiconductor package and its attachment to a printed circuit board. Such interference probably is caused by the physical separation between the copper substrate and die attach or molding compound and by the absence of any chemical bond between the antioxidant layer and die attach or molding compound. Benzotriazole is also known to be thermally unstable at the temperatures that are used for die attach adhesive curing and testing, which are typically at 170°C and above. The decomposition products and processes of benzotriazoles remain little
30 understood, and hence unpredictable in terms of their interference in the reliability of the lead frame packages.

SUMMARY OF THE INVENTION

35 [0004] This invention is directed to compounds that can be used as anti-oxidants for exposed metal surfaces, and also as adhesion promoters for adhesive, coating or encapsulant resins that are applied to the metal substrates. These compounds include triazine or isocyanurate compounds bearing reactive or polymerizable functional groups, polyfunctional cyanate esters, and polyfunctional blocked-isocyanates. Two attributes of these compounds that make them successful as adhesion promoters for resins applied on metal substrates are the presence of nitrogen with lone electron pairs, and the presence of functional groups that can react and form a chemical bond with the resins to be adhered to the metal substrate.

40 [0005] The lone electron pairs on the nitrogen will coordinate with the metal substrate: a direct attach in the case of cyanate esters, and a parallel attach in the case of triazines, isocyanurates, and blocked isocyanates by physical absorption. The lone electron pairs of the nitrogens further facilitate the coordination of the nitrogen atoms to the Cu substrates in the event any oxidation occurs to form Cu⁺ or Cu²⁺ ions or oxides.

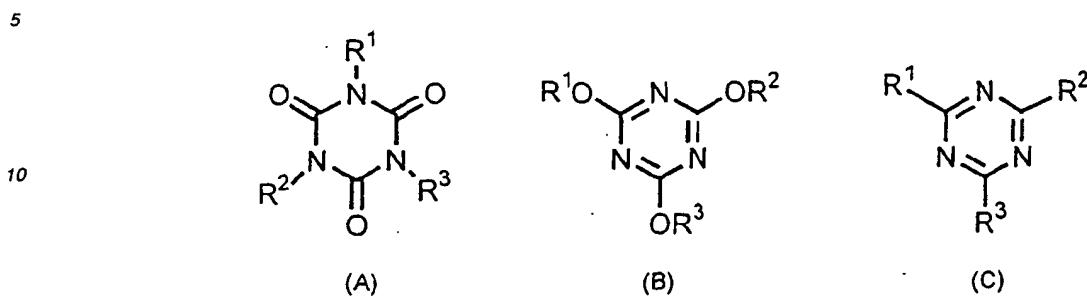
45 [0006] In the case of the triazines and isocyanurates, the functional group can be any reactive or polymerizable functional group, and preferably is an epoxy, allyl, vinylether, hydroxyl, acrylate or methacrylate group. In the case of the polyfunctional cyanate esters and isocyanates, these groups themselves are homo-polymerizable or are reactive with complementary reactive groups, such as, epoxy, carboxyl, hydroxyl and amine functionalities.

50 [0007] In a particular application, the compounds can be used in semiconductor packaging operations. The compounds are coated on metal leadframes, and through the nitrogen containing moieties, bond to the metal substrate; via the additional functional group on the compound, they react with adhesives, coatings or encapsulants used in the fabrication of semiconductor packages.

55 [0008] In a further embodiment, this invention relates to a metal leadframe and silicon die assembly, in which the metal leadframe is coated with a triazine or isocyanurate compound bearing reactive or polymerizable functional groups, a polyfunctional cyanate ester, or a polyfunctional blocked-isocyanate and the silicon die is attached to the leadframe with an epoxy, acrylate or bismaleimide based adhesive.

DETAILED DESCRIPTION OF THE INVENTION

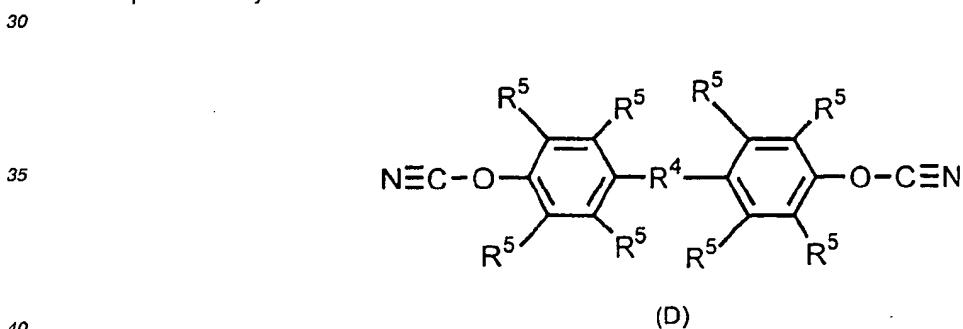
[0009] The triazine/isocyanurate compounds will have the structures:



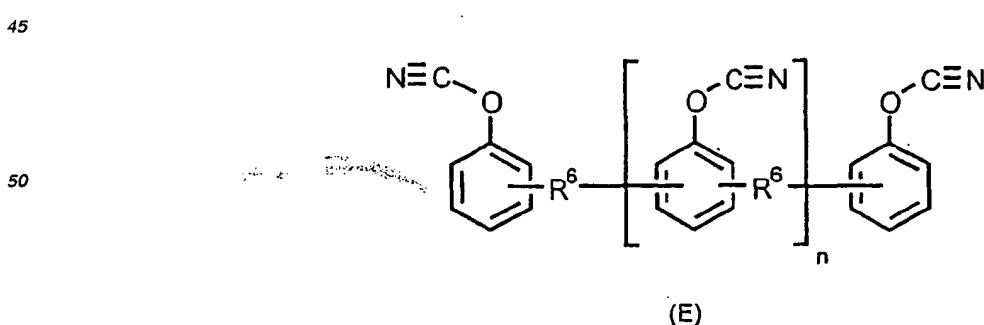
in which structures (A) and (B) represent isomers of isocyanurates; (C) represents triazines; and R¹, R², and R³ represent an organic moiety containing a reactive functionality, preferably an epoxy, allyl, amine, vinylether, hydroxyl, acrylate or methacrylate group. R¹, R², and R³ can be the same or different for each molecule. The three nitrogen atoms on the center ring of triazine and isocyanurate compounds provide parallel molecular access to the metal substrate.

[0010] Commercially available examples of such compounds include: 1,2,4-tris(2-hydroxyethyl)-1,2,4-triazine-3,5,6-(1H,2H,4H)-trione; 1,3,5-tris(cyanomethyl)hexahydro-1,3,5-triazine; 1,3,5-triacyclohexahydro-1,3,5-triazine; 1,3,5-tri-allyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; 1,3,5-triazine; 1,3,5-triazine-2,4,6-trithiol trisodium; 1,3,5-tris[3-(dimethylamino)propyl] hexahydro-1,3,5-triazine; 1,3,5-tris(2-hydroxyethyl)cyanuric acid; 2,4,6-tri(2-pyridyl)-1,3,5-triazine; 2,4,6-triallyoxy-1,3,5-triazine; 2,4,6-tris(2-pyridyl)-s-triazine; 2,6,4-trianilino-1,3,5-triazine; cyanuric acid potassium salt; melamine; oxonic acid; triallyl cyanurate; triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; trithiocyanuric acid; trithiocyanuric acid trisodium salt nonahydrate; and tris(2,3-epoxypropyl) isocyanurate.

[0011] The cyanate ester compounds will contain two or more cyanate ester functionalities. Preferred compounds are represented by the structures:

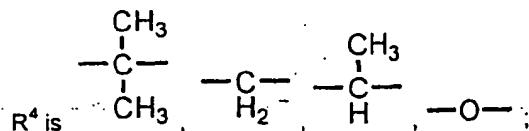


and

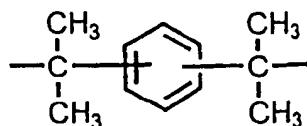


in which

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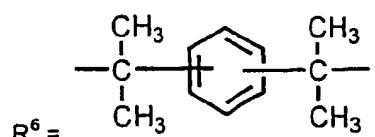
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 R^5 is H or CH₃;

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and

 n is 0.2 to 0.3

[0012] In one preferred embodiment, the cyanate ester will be difunctional. One of the cyanate ester functionalities will interact with the metal substrate, and the other cyanate ester functionality will react with a complementary reactive functionality on another resin present. Examples of other resins containing complementary reactive functionalities include cyanate esters, epoxies, amines, polyols, and phenols. Commercially available cyanate esters are available from Vantico, Lonza and Oakwood (such as L-10 and XU366).

[0013] The blocked isocyanates are adducts of a mono- or multifunctional isocyanate and a blocking group. The blocking group, before reaction with the isocyanate, contains an active hydrogen atom, such as from a hydroxyl or amine functionality, and will react with at least one of the isocyanate functionalities, although all the isocyanate functionalities on a molecule may be blocked.

[0014] Examples of suitable isocyanates include tolylene diisocyanate, hexane diisocyanate trimer, hexane diisocyanate biuret, isophorone diisocyanate, and isophorone diisocyanate trimer. Examples of suitable blocking groups include 3,5-dimethyl pyrazole, oxime, methylethyl ketoxime, ϵ -caprolactam, nonophenyl, and diethyl melonate. Commercially available blocked isocyanates are available from Baxenden Chemicals, Ltd (such as those sold under product numbers BI7770, 7772, 7773, 7779, 7673, 7952, 7985, 7986).

[0015] Below the unblocking temperature, the blocked isocyanate can bind to metal surfaces, in particular copper, via the nitrogens in the isocyanate functionality or via the nitrogens in the blocking group. Above the unblocking temperatures the released blocking groups can act as catalysts for polymerizations, for example, of epoxies or maleimides that may be present in other resins used in the manufacturing operations. The freed isocyanate groups can react with epoxy, hydroxyl and amine functionality that may be present in those resins.

[0016] If commercially available leadframes have been treated previously with benzotriazole, the benzotriazole preferably is removed before treating with the triazine/isocyanurates, cyanate esters or blocked isocyanates of this invention. The benzotriazole is removed with an acidic persulphate solution and a water rinse. The leadframe is treated with 1% sulfuric acid to activate the surface, which is then rinsed with water. Alternatively, the anti-oxidants described in this invention can be applied directly after etching (for patterning) or stamping (also for patterning) or electroplating of the circuitry on the leadframe, without the benzotriazole removal process described above.

[0017] If the anti-oxidant to be used is soluble in water, an aqueous solution is prepared at concentration ranges or 0.05 to 20% w/w (weight of solute in weight of solvent), preferably 0.1 to 10% w/w, and held at a temperature within the range of room temperature to 80°C. The leadframe is dipped into the solution at this temperature for a few minutes and rinsed with water at 60°C for 30 seconds to one minute. It is then dried under nitrogen at a temperature within the range of room temperature to 60°C for one hour.

[0018] If the anti-oxidant to be used is soluble in organic solvents, a solution is prepared at a concentration within the range of 0.05 to 20%, preferably 0.1 to 2% w/w, in acetone or methanol. The leadframe is given an acetone or methanol rinse and then is dipped in the anti-oxidant solution for a few minutes, rinsed with acetone or methanol, and dried under nitrogen for one hour at room temperature.

[0019] In another embodiment, this invention comprises the coated lead frame and a silicon chip adhered to the lead frame and assembled into a semiconductor package. Methods for the manufacture of semiconductor packages are well known in the art. An exemplary method consists of the following. The substrate for holding the semiconductor chip within the semiconductor package is a metal leadframe, in many packages, a copper leadframe, which can be described as a frame with a center area within the frame containing a paddle on which the silicon chip will be mounted. A plurality of metal leads extend from ends integral with the frame to other ends adjacent to the center region of the frame and the chip paddle.

[0020] A conductive adhesive is dispensed onto the chip paddle, a silicon chip is contacted with the adhesive, using light pressure and/or heat to soften the adhesive. The assembly is cured, typically in an atmosphere of dry nitrogen, at an appropriate temperature and time to effect cure for the specific adhesive used. For example, a typical curing schedule for an epoxy is to ramp from room temperature to 175°C within 30 minutes and dwell at this temperature for additional 15 minutes. Such curing schedules will be known to those skilled in the art or supplied by the manufacturer of the adhesive.

[0021] Active terminals on the surface of the silicon chip are then connected to the active terminals on the surface of the metal leadframe with a fine metal wire or ribbon in an automated operation known as wire-bonding. The wire bonded assembly is then protected by encapsulation in a polymeric material. Encapsulation is performed by a transfer molding process, in which the assembly is loaded into a mold cavity, constrained, and the polymeric encapsulant transferred from a reservoir into the cavity under pressure, and finally cured.

[0022] In order to benefit from the inventive anti-oxidative coating on the leadframe, the conductive adhesive attaching the semiconductor chip to the leadframe paddle preferably is reactive with the anti-oxidative coating. That is, the adhesive will have a reactive functionality complementary to the reactive functionality on the triazine compound or isocyanurate compound, if either of those is the coating material used, or will have a functionality reactive to cyanate ester or isocyanate functionality, if either of those is the coating material used.

[0023] For use with the triazine or isocyanurate coating material, the adhesive for attaching the chip to the substrate should be reactive with whatever polymerizable functional group is on the triazine or isocyanurate. Such complementary reactive functionalities are well known by those skilled in the art. For example, in those cases in which the polymerizable functional group is an epoxy, allyl, vinyl ether, hydroxyl, acrylate or methacrylate group, the conductive adhesive may be selected from epoxies, electron donor resins (for example, vinyl ethers, vinyl silanes, thiol-enes, and resins that contain carbon to carbon double bonds attached to an aromatic ring and conjugated with the unsaturation in the aromatic ring, such as compounds derived from cinnamyl and styrenic starting compounds), and, electron acceptor resins (for example, fumarates, maleates, acrylates, and maleimides). One skilled in the art will understand which functionalities are reactive with each other.

[0024] For use with polyfunctional cyanate ester and blocked isocyanate coatings, the conductive adhesive may be selected from cyanate esters, isocyanates, epoxies, and with other resins containing carboxyl, hydroxyl or amine functionalities. Suitable curable conductive resins meeting these criteria are known to those skilled in the art.

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EXAMPLES

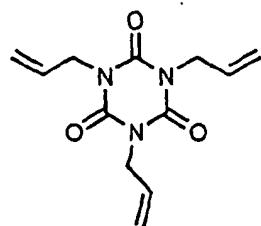
[0025] In the following examples, adhesives were dispensed onto copper leadframe substrates whose surfaces were treated to remove benzotriazole as described above in this specification. Silicon dies were then attached onto the lead frames with an adhesive and the adhesive was cured. (The exact curing profile depended on the composition used. Ascertaining the appropriate curing profile is within the expertise of one skilled in the art, or will be as disclosed by the supplier.) Leadframes as received from the manufacturer were used as the controls.

[0026] The cured assemblies were subjected to 85°C/85% relative humidity for 48 hours, after which the die was sheared from the copper leadframe at 90 degrees with a Dage 2400-PC Die Shear Tester at 260°C (hot-wet die shear-hwds). The die shear strength values as well as the percent cohesive failure were measured and are reported.

[0027] EXAMPLE 1. Two silver filled adhesives were prepared, one comprising an epoxy resin (EPO), and the other comprising a bismaleimide and epoxy blend (BMI/EPO). The adhesives were used to attach silicon dies to copper leadframes and tested for hot-wet die shear strength and percent cohesive failure as described above. The anti-oxidants used to coat the leadframes were the following labeled A through D:

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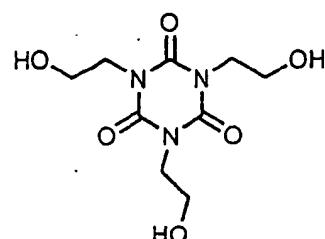
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Antioxidant A

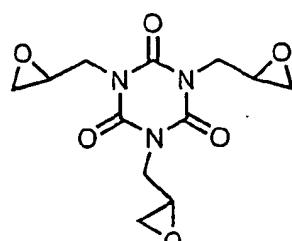
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Antioxidant B

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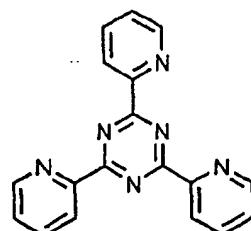


30

Antioxidant C

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Antioxidant D

[0028] Ten assemblies for the control and for each triazine/isocyanurate antioxidant were prepared for each adhesive and the results pooled and averaged. The results of the hot-wet die shear strength (HWDS) test in Kg force and percent cohesive failure (% coh) are reported in the following table:

50

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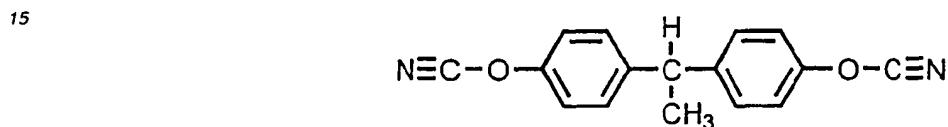
	No treatment	Antioxidant A	Antioxidant B	Antioxidant C	Antioxidant D
EPO					
HWDS kg	4.0	10.1	10.6	11.1	9.9
% coh	10	98	95	70	85

(continued)

	No treatment	Antioxidant A	Antioxidant B	Antioxidant C	Antioxidant D
5	BMI/EPO				
10	HWDS kg	8.9	16.2	15.5	15.2
	% coh	30	70	45	60
					40

[0029] The results indicate that the use of triazine and isocyanurate based anti-oxidants to coat metal improves the performance of adhesives on that metal substrate.

[0030] EXAMPLE 2. The same adhesives and procedures for hot-wet die shear strength and percent cohesive failure were used on leadframes coated with a cyanate ester having the following structure:

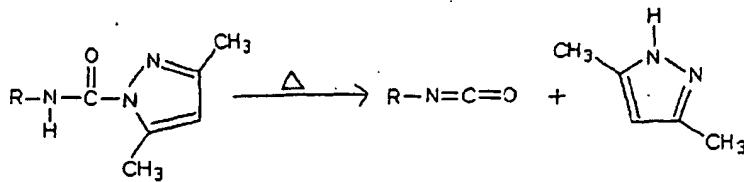


20 [0031] Ten assemblies for the control and for the cyanate ester antioxidant were prepared for each adhesive and the results pooled and averaged. The results are reported in the following table and indicate that the use of the cyanate ester based anti-oxidant (CE) to coat metal improves the performance of adhesives on that metal substrate.

	No treatment	Antioxidant CE1	Antioxidant CE2
25	EPO		
30	HWDS kg	7.6	9.9
35	% coh	60	90
			80
	BMI/EPO		
	HWDS kg	2.3	8.6
	% coh	0	30
			40



45 [0032] EXAMPLE 3. The same adhesives and procedures for hot-wet die shear strength and percent cohesive failure were used on leadframes coated with blocked isocyanates (BI) having the following structure: Where RN(H)C=O represents the isocyanate molecule after being adducted to the blocking group. Suitable starting isocyanates include, but are not limited to, tolylene diisocyanate, hexane diisocyanate trimer, hexane diisocyanate biuret, isophorone diisocyanate, and isophorone diisocyanate trimer. BL represents a blocking group after being adducted to the starting isocyanate. Suitable starting blocking groups include, but are not limited to; 3,5-dimethyl pyrazole, oxime, methylethyl ketoxime, ϵ -caprolactam, nonophenyl, and diethyl melonate. These blocked isocyanates are stable at room temperature, and will release the BL group at the unblocking temperature. For instance, 3,5-dimethyl pyrazole blocked isocyanates, as blocking agents, can be released at 120°C:



10 [0033] Ten assemblies for the control and for each blocked isocyanate antioxidant were prepared for each adhesive and the results pooled and averaged. The results are reported in the following table and indicate that the use of the blocked isocyanate based anti-oxidant (Bl) to coat metal improves the performance of adhesives on that metal substrate.

15

	No treatment	Antiox Bl						
EPO								
HWDS Kg	7.5	7.5	8.0	9.1	7.5	8.3	8.3	9.0
% coh	60	95	95	95	90	95	90	95
BMI/EP								
HWDS Kg	9.2	16.1	14.3	13.4	12.0	11.2	13.0	12.9
% coh	5	70	50	60	35	35	40	35

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Claims

30 1. A metal substrate or a metal surface coated with a solution of
 (i) a triazine or isocyanurate compound containing a polymerizable functionality,
 (ii) a cyanate ester compound, or
 (iii) a blocked isocyanate compound.

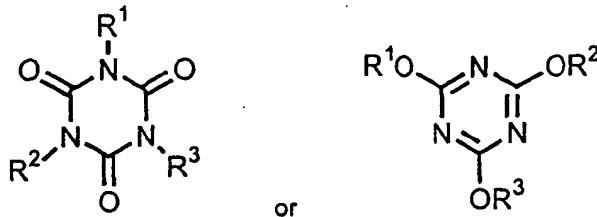
35 2. The metal substrate or metal surface according to claim 1 in which the metal substrate is a copper coated leadframe.

40 3. The metal substrate or metal surface according to claim 1 in which the solution is an aqueous solution with a concentration range from 0.05 to 20% w/w.

45 4. The metal substrate or metal surface according to claim 3 in which the solution is an aqueous solution with a concentration range from 0.1 to 10% w/w.

50 5. The metal substrate or metal surface according to claim 1 in which the solution is an organic solution with a concentration range from 0.1 to 2% w/w.

55 6. The metal substrate or metal surface according to claim 1 in which the triazine has the structure



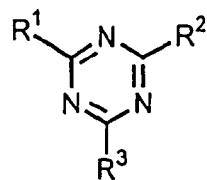
in which R¹, R², and R³ represent an organic moiety containing an epoxy, allyl, amine, vinylether, hydroxyl, acrylate

or methacrylate group.

7. The metal substrate or metal surface according to claim 1 in which the isocyanurate has the structure

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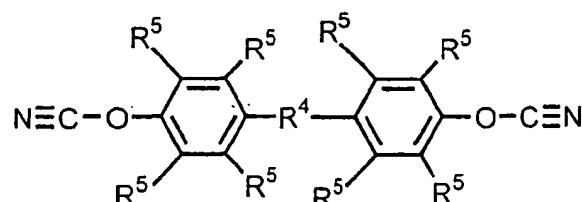
in which R¹, R², and R³ represent an organic moiety containing an epoxy, allyl, amine, vinylether, hydroxyl, acrylate or methacrylate group.

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8. The metal substrate or metal surface according to claim 1 in which the cyanate ester has the structure

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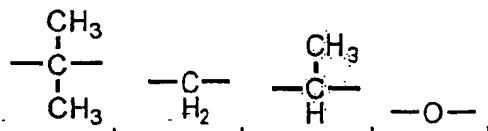
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in which R⁴ is

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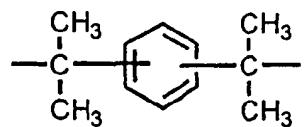
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or

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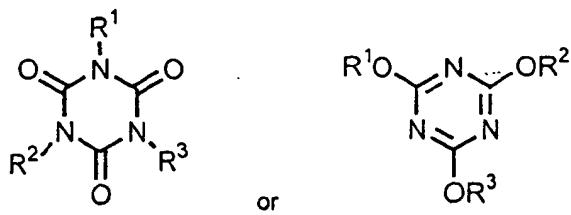
and

R⁵ is H or CH₃.

9. The metal substrate or metal surface according to claim 1 in which the blocked isocyanate compound is an adduct of an isocyanate selected from the group consisting of tolylene diisocyanate, hexane diisocyanate trimer, hexane diisocyanate biuret, isophorone diisocyanate, and isophorone diisocyanate trimer with a blocking group selected from the group consisting of 3,5-dimethyl pyrazole, oxime, methylethyl ketoxime, ϵ -caprolactam, and diethyl malonate.

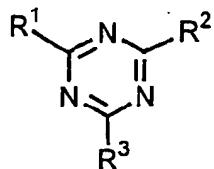
55 10. A semiconductor package comprising a metal leadframe and a semiconductor chip adhered to the metal leadframe with an adhesive in which the metal leadframe is coated with a solution of a triazine or isocyanurate compound bearing a polymerizable functionality, and the adhesive contains a functionality reactive with the polymerizable functionality on the triazine or isocyanurate compound.

11. The semiconductor package according to claim 10 in which the triazine has the structure



in which R¹, R², and R³ represent an organic moiety containing an epoxy, allyl, amine, vinylether, hydroxyl, acrylate or methacrylate group.

15 12. The semiconductor package according to claim 10 in which the isocyanurate has the structure

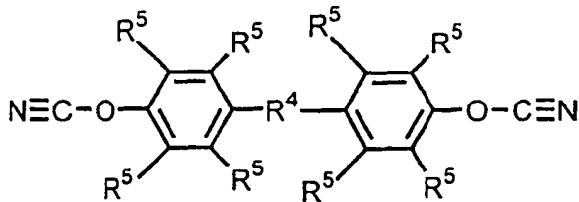


25 in which R¹, R², and R³ represent an organic moiety containing an epoxy, allyl, amine, vinylether, hydroxyl, acrylate or methacrylate group.

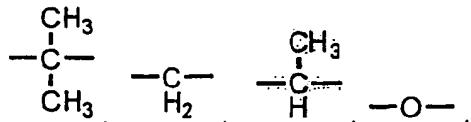
30 13. The semiconductor package according to claim 10 in which the adhesive is selected from the group consisting of epoxies, vinyl ethers, vinyl silanes, thiol-enes, resins derived from cinnamyl and styrenic starting compounds, fumarates, maleates, acrylates, methacrylates, and maleimides.

35 14. A semiconductor package comprising a metal leadframe and a semiconductor chip adhered to the metal leadframe with an adhesive in which the metal leadframe is coated with a solution of a cyanate ester compound or a blocked isocyanate compound, and the adhesive is selected from the group consisting of cyanate esters, isocyanates, epoxies, and resins containing carboxyl, hydroxyl or amine functionalities.

15. The semiconductor package according to claim 14 in which the cyanate ester has the structure

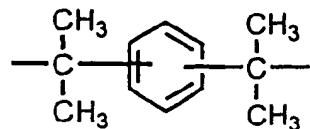


in which R⁴ is



or

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and R⁵ is H or CH₃.

10 16. The semiconductor package according to claim 14 in which the blocked isocyanate is an adduct of an isocyanate selected from the group consisting of tolylene diisocyanate, hexane diisocyanate trimer, hexane diisocyanate biuret, isophorone diisocyanate, and isophorone diisocyanate trimer with a blocking group selected from the group consisting of 3,5-dimethyl pyrazole, oxime, methylethyl ketoxime, ϵ -caprolactam, nonylphenol and diethyl malonate.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 02 3562

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
X	US 5 723 523 A (ENGELHARDT ET AL) 3 March 1998 (1998-03-03) * column 1, line 17 - line 25 * * column 2, line 59 - column 4, line 17; claim 1 *	1,7	C08K5/3492 C08G18/80 H01L23/52
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